

We Claim:

1. A method of making a fluorinated precursor of a superconducting ceramic, said method comprises:

- a) providing a solution comprising a rare earth salt, an alkaline earth metal salt and a copper salt;
- b) spraying said solution onto a substrate to provide a film-covered substrate; and
- c) heating said film-covered substrate in an atmosphere containing fluorinated gas to provide said fluorinated precursor.

2. A method according to Claim 1 wherein said solution has a pH in the range of approximately 1 to 5.

3. A method according to Claim 1 further comprising dispersing said solution in a carrier gas before spraying said solution on said substrate, wherein said carrier gas comprises an inert gas.

4. A method according to Claim 3 wherein said inert gas is selected from the group consisting of nitrogen, argon, helium and mixtures thereof.

5. A method according to Claim 3 wherein said carrier gas further comprises oxygen.

6. A method according to Claim 1 further comprising heating said substrate before spraying said solution on said substrate.

7. A method according to Claim 1 wherein said rare earth salt is selected from the group consisting of a yttrium (Y) salt, a neodymium (Nd) salt, a, a ytterbium (Yb) salt, an europium (Eu) salt, a gadolinium (Gd) salt, a dysprosium (Dy) salt, a holmium (Ho) salt, an erbium (Er) salt, a lanthanum (La) salt, a lutetium (Lu) salt, a samarium (Sm) salt, a thulium (Tm) salt, and mixtures thereof.

8. A method according to Claim 6 wherein said rare earth salt is a yttrium (Y) salt.

9. A method according to Claim 7 wherein said rare earth salt is selected from the group consisting of a rare earth nitrate, a rare earth acetate and mixtures thereof.

10. A method according to Claim 7 wherein said rare earth salt is selected from the group consisting of a rare earth sulfate, a rare earth chloride, a rare earth bicarbonate and mixtures thereof.

11. A method according to Claim 1 wherein said salt of an alkaline earth metal is selected from the group consisting of a magnesium (Mg) salt, a calcium (Ca) salt, a strontium (Sr) salt and a barium (Ba) salt and mixtures thereof.

12. A method according to Claim 11 wherein said salt of an alkaline earth metal is a barium (Ba) salt.

13. A method according to Claim 12 wherein said barium (Ba) salt is selected from the group consisting of a barium nitrate, a barium acetate and mixtures thereof.

14. A method according to Claim 12 wherein said barium salt is selected from the group consisting of a barium sulfate, a barium chloride and mixtures thereof.

15. A method according to Claim 1 wherein said copper salt is selected from the group consisting of a copper nitrate, a copper acetate and mixtures thereof.

16. A method according to Claim 1 wherein said copper salt is selected from the group consisting of a copper sulfate, a copper sulfide, a copper chloride and mixtures thereof.

17. A method according to Claim 1 wherein said substrate is selected from the group consisting of a single crystalline ceramic, polycrystalline ceramic, a single crystal and a metal.

18. A method according to Claim 17 wherein said substrate is selected from the group consisting of SrTiO₃, LaAlO₃, zirconia, CeO₂, Y₂O₃, MgO, and SrRuO₃.

19. A method according to Claim 17 further comprising placing a buffer layer on said metal substrate before spraying said solution.

20. A method according to Claim 1 wherein said fluorinated gas is selected from the group consisting of CHF₃, CH₂F₂, CH₃F, CHF₂CHF₂ (HFC 134), CHF₂CF₃ (HFC 125), CHF₂CH₃ (HFC 152a), CF₃CH₂F (HFC 134a), CH₃CF₃, CH₂FCH₃, CHF₂CH₂F, CH₂FCH₂F, CF₃CH₂CF₃ (HFC 236fa), a fluorinated propane, a fluorinated propylene, a fluorinated ethylene and mixtures thereof.

21. A method according to Claim 1 wherein said fluorinated gas comprises

CF₃CH₂F (HFC 134a).

22. A method according to Claim 1 wherein said solution comprises Y, Ba and Cu in a ratio of 1:2:0.5.

23. A method according to Claim 1 further comprising subjecting said solution to a high voltage Corona discharge before or during the spraying of said solution on said substrate.

24. A method according to Claim 23 wherein said solution comprises Y, Ba and Cu in a ratio of 1:2:3.5.

25. A method according to Claim 1 where said atmosphere containing fluorinated gas is subject to a high voltage electrical discharge.

26. A method according to Claim 1 further comprising transforming the fluorinated precursor into a crystalline superconducting ceramic.

27. A fluorinated precursor of a superconducting ceramic produced by a method comprising:

- a) providing a solution of a rare earth salt, an alkaline earth metal salt and a copper salt;
- b) spraying said solution onto a substrate to provide a film-covered substrate; and
- c) heating said film-covered substrate in an atmosphere containing fluorinated gas to produce said fluorinated precursor film.

28. A film according to Claim 27, wherein said film is a $\text{YBa}_2\text{Cu}_3\text{O}_y$ film.
29. A film according to Claim 27, wherein said film has a critical current density measured at 77 K of about 0.1 MA/cm^2 or greater in zero magnetic field.
30. A method of making a fluorinated precursor of a superconducting ceramic, said method comprising:
- a) providing a solution of a rare earth salt, an alkaline earth metal salt and a copper salt; and
 - b) spraying said solution and fluorinated gas onto a substrate to provide said fluorinated precursor.
31. A method according to Claim 30 wherein said solution has a pH in the range of approximately 1 to 5.
32. A method according to Claim 30 further comprising dispersing said solution in a carrier gas before spraying said solution on said substrate, wherein the carrier gas comprises an inert gas.
33. A method according to Claim 32 where said inert gas is selected from the group consisting of nitrogen, argon, helium and mixtures thereof.
34. A method according to Claim 30 wherein said rare earth salt is selected from the group consisting of a yttrium (Y) salt, a neodymium (Nd) salt, a, a ytterbium (Yb) salt, an europium (Eu) salt, a gadolinium (Gd) salt, a dysprosium (Dy) salt, a holmium (Ho) salt, an erbium (Er) salt, a lanthanum (La) salt, a lutetium (Lu) salt, a samarium (Sm) salt, a thulium (Tm) salt, and mixtures thereof.

35. A method according to Claim 30 wherein said rare earth salt is a yttrium (Y) salt.

36. A method according to Claim 30 wherein said rare earth salt is selected from the group consisting of a rare earth nitrate, a rare earth acetate and mixtures thereof.

37. A method according to Claim 30 wherein said rare earth salt is selected from the group consisting of a rare earth sulfate, a rare earth chloride, a rare earth bicarbonate and mixtures thereof.

38. A method according to Claim 30 wherein said salt of an alkaline earth metal is selected from the group consisting of a magnesium (Mg) salt, a calcium (Ca) salt, a strontium (Sr) salt, a barium (Ba) salt and mixtures thereof.

39. A method according to Claim 30 wherein said salt of an alkaline earth metal is a barium (Ba) salt.

40. A method according to Claim 39 wherein said barium (Ba) salt is a barium nitrate, barium acetate or mixtures thereof.

41. A method according to Claim 39 wherein said barium (Ba) salt is a barium sulfate, a barium chloride or mixtures thereof.

42. A method according to Claim 30 wherein said copper salt is a copper nitrate, a copper acetate or mixtures thereof.

43. A method according to Claim 30 wherein said copper salt is a copper

sulfate, a copper sulfide or mixtures thereof.

44. A method according to Claim 30 wherein said substrate is selected from the group consisting of a single crystalline ceramic, polycrystalline ceramic, a single crystal and a metal.

45. A method according to Claim 44 wherein said substrate is selected from the group consisting of SrTiO_3 , LaAlO_3 , zirconia, CeO_2 , Y_2O_3 and MgO , SrRuO_3 .

46. A method according to Claim 30 further comprising placing a buffer layer on said metal substrate before spraying said solution.

47. A method according to Claim 30 wherein said fluorinated gas is selected from the group consisting of CHF_3 , CH_2F_2 , CH_3F , CHF_2CHF_2 (HFC 134), CHF_2CF_3 (HFC 125), CHF_2CH_3 (HFC 152a), $\text{CF}_3\text{CH}_2\text{F}$ (HFC 134a), CH_3CF_3 , CH_2FCH_3 , $\text{CHF}_2\text{CH}_2\text{F}$, $\text{CH}_2\text{FCH}_2\text{F}$, $\text{CF}_3\text{CH}_2\text{CF}_3$ (HFC 236fa), a fluorinated propane, a fluorinated propylene, a fluorinated ethylene and mixtures thereof.

48. A method according to Claim 30 wherein said fluorinated gas comprises $\text{CF}_3\text{CH}_2\text{F}$ (HFC 134a).

49. A method according to Claim 30 further comprising transforming the fluorinated precursor into a crystalline superconducting ceramic.

50. A method according to Claim 30 where said atmosphere containing fluorinated gas is subject to an electrical discharge.

51. A fluorinated precursor film produced by a method comprising:
- a) providing a solution of a rare earth salt, an alkaline earth metal salt and a copper salt; and
 - b) spraying said solution onto a substrate in an atmosphere containing fluorinated gas to provide said fluorinated precursor film.
52. A film according to Claim 51, wherein said film is a $\text{YBa}_2\text{Cu}_3\text{O}_y$ film.
53. A film according to Claim 51, wherein said film has a critical current density measured at 77 K of about 0.1 MA/cm^2 or greater in zero magnetic field.
54. A method of increasing the quality of a precursor film, the method comprising:
- heat treating said precursor film at atmospheric or sub-atmospheric pressure in the presence of fluorinated gas and oxygen to produce a resultant precursor film.
55. A method according to Claim 54 further comprising heating said resultant precursor film in an atmosphere comprising nitrogen, water vapor and oxygen at atmospheric or sub-atmospheric pressure to produce a crystalline film.
56. A method according to Claim 54 wherein heat treatment comprises heating a precursor film to a temperature of about 400°C to about 800°C for about a half an hour to about three hours at about 1 to 760 Torr.
57. A method of inhibiting the conversion of a fluorinated precursor film into a crystalline film, wherein the film comprises rare earth metal, alkaline earth metal cuprate, said the method comprising adding a small amount of fluorinated gas during a heat treatment process by which a precursor film is to be converted into a crystalline film.

58. A method according to Claim 57 wherein the fluorinated gas is added at a pressure of approximately 10 milliTorr or greater during said heat treatment process.